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Synthesis of Functional Phosphates $[P(C_2F_5)_3F_2X]^-$ from the Phosphorane Adduct $[P(C_2F_5)_3F_2(dmap)]$

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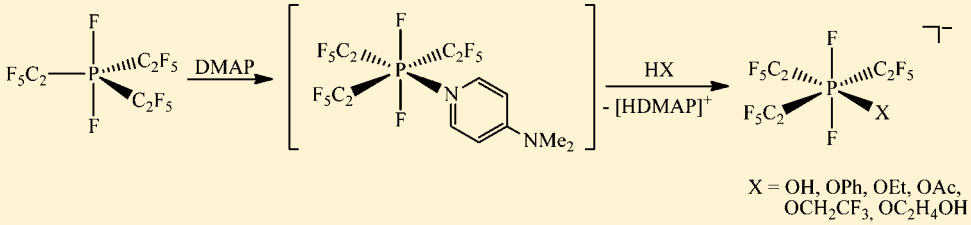
Supporting Information



ABSTRACT: Weakly coordinating anions (WCAs) are of great academic as well as industrial interest. To advance the fluoroalkyl phosphate anion $[P(C_2F_5)_3F_3]^-$, which is ideally suited for technical applications, functional substituents X are attached to the Lewis acid $(C_2F_5)_3PF_2$. In keeping with this, the reaction of $(C_2F_5)_3PF_2$ with 4-(dimethylamino)pyridine (DMAP) yields the corresponding adduct $[P(C_2F_5)_3F_2(dmap)]$. Treatment of this adduct with Brønsted acids (HX) leads to the selective formation of the corresponding phosphate anions $[P(C_2F_5)_3F_2X]^-$ by trapping the proton with the liberated base DMAP. In this way, OH functions can be transformed in one step into WCAs, slightly increasing the coordination properties of the corresponding anion. An ion exchange to the corresponding $[PPh_4]$ salts results in solids, whereas the corresponding imidazolium salts are obtained as room-temperature ionic liquids.

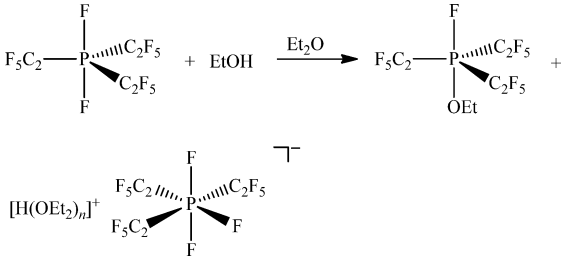
INTRODUCTION

Weakly coordinating anions[1] are required for the application in ionic liquids, as lithium ion or proton conducting materials, and for the stabilization of reactive or unstable cations. Thereby, $[PF_6]^-$ is one of the most commonly used anions. It is employed as $Li[PF_6]$ in electrolytes for lithium ion batteries[2] as well as in combination with organic cations like imidazolium derivatives as ionic liquid.[3,4] Disadvantageously, the PF bond is sensitive toward hydrolysis. The coordination of a proton to a fluorine atom weakens the PF bond, facilitating elimination of HF and the subsequent reaction of PF_5 with water.[5,6] To circumvent this obstacle, perfluoroalkyl substituents are introduced to the phosphate anion to enhance the stability toward hydrolysis. Fluoroperfluoroalkyl phosphate derivatives have been known for about 40 years.[7]

The technical product $(C_2F_5)_3PF_2$, which is produced by means of electrochemical fluorination of trialkylphosphanes,[8] reacts with LiF to the corresponding salt $Li[P(C_2F_5)_3F_3]$ (LiFAP) (FAP = fluoroalkyl phosphate). LiFAP is hydrolytically much more stable than $Li[PF_6]$ and exhibits an electrochemical stability up to 5 V versus Li/Li^+.[9] Additionally, the FAP anion is ideally suited for the application in ionic liquids. For this purpose, $(C_2F_5)_3PF_2$ is converted selectively in an aqueous HF solution to the corresponding phosphoric acid $[H(OH_2)_n][P(C_2F_5)_3F_3]$,[10] which serves as a starting material for the synthesis of a broad variety of ionic liquids. Salts with imidazolium derivatives as cations, for example, are hydrophobic. The water uptake is up to 10 times lower than that of comparable hexafluorophosphates, and also the viscosity is significantly reduced.[11]

A modification of the FAP anion could be achieved by the addition of functional substituents X to the phosphorane moiety $(C_2F_5)_3PF_2$. It is conceivable that the chemical properties of the resulting weakly coordinating anions can be controlled by the nature of X and ideally tuned to a desired application.

The selective synthesis of such functionalized phosphates proved to be quite difficult and strongly depends on the chosen reaction conditions. Thus, the preparation of difluorohydroxotris-(pentafluoroethyl)phosphate, $[P(C_2F_5)_3F_2OH]^-$, by the direct reaction of $(C_2F_5)_3PF_2$ with an aqueous solution of a hydroxide salt, requires the strict adherance to several conditions like temperature, concentration and solvent.[12] Our previous investigations have shown that a direct synthesis of an alkoxyphosphate $[P(C_2F_5)_3F_2OR]^-$ (R = alkyl, aryl) is not possible, either, by the reaction of $(C_2F_5)_3PF_2$ with ethanol nor by the reaction with alkali metal alcoholates.



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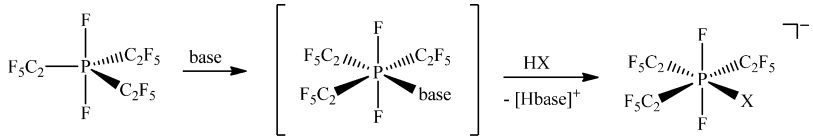
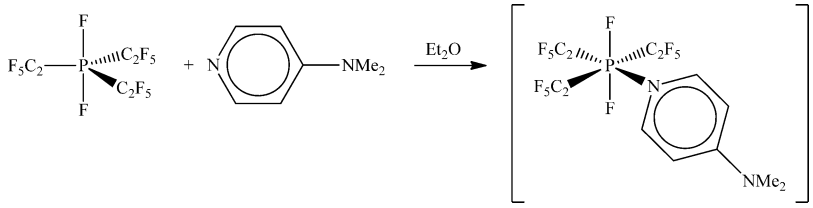
Scheme 1. Synthetic Strategy for Functionalized Difluorotris(pentafluoroethyl)phosphates $[P(C_2F_5)_3F_2X]^-$



Scheme 2. Synthesis of $[P(C_2F_5)_3F_2(dmap)]$



Therefore, the development of a new protocol that enables a selective synthesis of $[P(C_2F_5)_3F_2X]^-$ derivatives is highly desirable. One possible synthetic strategy is based on adducts of the phosphorane $(C_2F_5)_3PF_2$ with basic molecules. Subsequently, the base could abstract the proton from Brønsted acids (HX), affording the selective formation of functionalized derivatives $[P(C_2F_5)_3F_2X]^-$ (see Scheme 1).

Muetterties et al. described adducts of pentafluorophosphorane with ethers, sulfoxides, and amines,[13] and Sheldrick succeeded in 1973 in the first structural characterization of a pyridine adduct. The solid-state structure of $[PF_5(py)]$ exhibits an octahedrally coordinated phosphorus atom.[14]

RESULTS AND DISCUSSION

In analogy to PF_5, which forms a solid pyridine adduct (mp 179−182 °C),[13] the reaction of $(C_2F_5)_3PF_2$ with 4-(dimethylamino)pyridine (DMAP) in diethyl ether selectively leads to the adduct $[P(C_2F_5)_3F_2(dmap)]$ (cf. Scheme 2) as a colorless solid in a yield of 97%.[15] The product can be handled in air for a short time and melts at 150−153 °C.

The addition of a nucleophile X^- to $(C_2F_5)_3PF_2$ generally may yield three different stereoisomers $[P(C_2F_5)_3F_2X]^-$. Two isomers are distinguishable by NMR spectroscopy (cf. Figure 1).

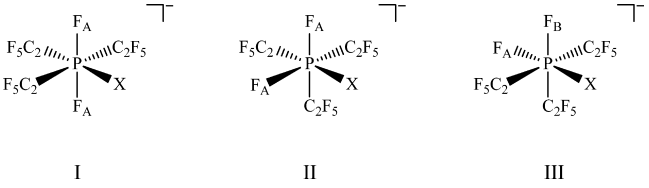


Figure 1. Possible stereoisomers for $[P(C_2F_5)_3F_2X]^-$ derivatives.

Form **III** exhibits two chemically inequivalent fluorine atoms F_A and F_B, whereas in isomers **I** and **II** both phosphorus-bound fluorine atoms are equivalent.

Isomers **I** and **II**, where the pentafluoroethyl groups are oriented meridionally (**I**) and facially (**II**), cannot be discriminated that easily. The chemical shift of the fluorine atoms F_A in the ^{19}F NMR spectrum, however, provides important structural information. The fluorine atoms F_A in **I** display chemical shifts in the range of $\delta(^{19}F) = -80$ to -110, whereas the resonances for the chemically equivalent fluorine atoms F_A in conformer **II** are usually observed at a significantly lower field. A known example for this argument is $[P(C_2F_5)_3F_3]^-$, which occurs in the meridional form **I**/**III** as well as in the facial form **II** (cf. Figure 1).[10]

The ^{19}F NMR spectrum of $[P(C_2F_5)_3F_2(dmap)]$ reveals only one resonance for the fluorine atoms F_A bound directly to the phosphorus atom, which agrees with the meridional conformer **I** as well as the facial conformer **II**. The chemical shift of the fluorine atoms F_A at $\delta(^{19}F) = -99.4$ supports a trans configuration of the fluorine atoms and therefore isomer **I**, which is also present in the solid state.

$[P(C_2F_5)_3F_2(dmap)]$ crystallizes in the monoclinic space group $P2_1/c$ with four formula units per unit cell.[16] The asymmetric unit is represented by one $[P(C_2F_5)_3F_2(dmap)]$ unit. The plane of the pyridine ring is nearly parallel with the F1−P1−F2 vector. In contrast, the plane of the pyridine ring in $[PF_5(py)]$ is rotated by about 45° with respect to comparable F−P−F vectors, which was explained by intermolecular F−H contacts.[14] The length of the coordinative N−P bond is, at 190.9 pm, comparable to that observed for $[PF_5(py)]$ (189.8 pm) and is significantly shorter than the sum of the van der Waals radii of 350 pm.[17] The bond lengths and angles of the DMAP substituent match those of free DMAP (cf. Figure 2).

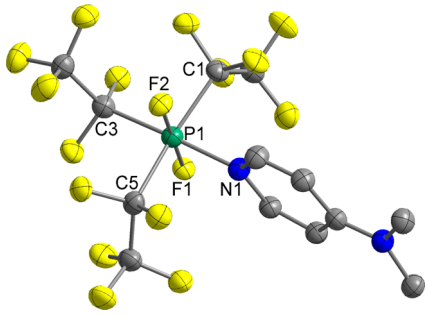


Figure 2. Molecular structure and numbering scheme of $[P(C_2F_5)_3F_2(dmap)]$ in the solid state. H atoms are omitted for clarity. 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: P1−F1 162.3(1), P1−F2 162.5(1), P1−N1 190.9(1), P1−C1 197.5(2), P1−C3 198.1(2), P1−C5 197.2(2); F1−P1−F2 179.5(1), C1−P1−C5 171.1(1).

$(C_4F_9)_3PF_2$ reacts with DMAP in diethyl ether to give the desired adduct $[P(C_4F_9)_3F_2(dmap)]$. Our attempt to isolate the adduct simply by removing the solvent in vacuum was not successful. The compound $[P(C_4F_9)_3F_2(dmap)]$ decomposes and trifluorotris(nonafluorobutyl)phosphate, $[P(C_4F_9)_3F_3]^-$, is formed among other side products.

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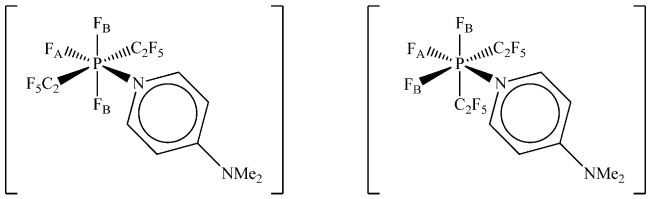
$(C_2F_5)_2PF_3$ reacts with DMAP, but $[P(C_2F_5)_2F_4]^-$ is formed as a side product. The desired product $[P(C_2F_5)_2F_3(dmap)]$ could be detected by NMR spectroscopic methods with a conversion of 40%. The resonance of $[P(C_2F_5)_2F_3(dmap)]$ in the ^{31}P NMR spectrum is detected in the expected range and exhibits a $^1J_{P,FA}$ coupling constant of 940 Hz as well as a $^1J_{P,FB}$ coupling constant of 996 Hz. The coupling to the fluorine atoms of the CF_2 units results in a quintet. For the fluorine atoms of the pentafluoroethyl groups, in the CF_3 range as well as in the CF_2 range, only one resonance is detected in the ^{19}F NMR spectrum. On the basis of the chemical equivalence of the pentafluoroethyl groups, it is not possible to distinguish between the two structures depicted in Figure 3 by NMR spectroscopy.

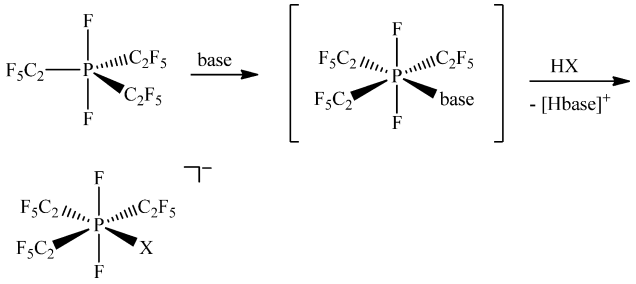


OC-6-21 I *OC*-6-33 III

Figure 3. Possible isomers of $[P(C_2F_5)_2F_3(dmap)]$.

The chemical shift of the fluorine atoms F_B in the ^{19}F NMR spectrum at $\delta = -83.1$ is in favor of a trans conformation and therefore supports isomer **I**.

The adduct $[P(C_2F_5)_3F_2(dmap)]$ was synthesized as a precursor for various $[P(C_2F_5)_3F_2X]^-$ derivatives via the reaction with Brønsted acids HX.[15]



To generate the hydroxophosphate ion $[P(C_2F_5)_3F_2OH]^-$, $[P(C_2F_5)_3F_2(dmap)]$ is dissolved in diethyl ether and treated with an excess of water. NMR monitoring discloses the selective formation of $[HDMAP][P(C_2F_5)_3F_2OH]$. Attempts to isolate the salt by removing the solvent in vacuum were not successful.

After a cation exchange with $[PPh_4]Cl$ and the subsequent aqueous workup, the hydroxophosphate salt $[PPh_4][P(C_2F_5)_3F_2OH]$ was isolated as a colorless solid (mp 139 °C) in 94% yield.

The $^1J_{P,F}$ coupling constant decreases significantly going from $[P(C_2F_5)_3F_2(dmap)]$ to $[P(C_2F_5)_3F_2OH]^-$ from $J = 986$ to 846 Hz. In the ^1H NMR spectrum, the OH proton gives rise to a signal at 5.1 ppm; in deuterated tetrahydrofuran (THF-d_8), acetone-d_6, and $CDCl_3$, only a triplet splitting due to a $^3J_{H,F}$ coupling of $J = 14$ Hz is observed. In CD_3CN, however, an additional doublet splitting due to the $^2J_{H,P}$ coupling of $J = 3$ Hz is detected, which is supported by the phosphorus decoupled ^1H NMR experiment. For the fluorine atoms bonded directly to the phosphorus atom (F_A), only one resonance appears in the ^{19}F NMR spectrum. Because of the chemical shift of $\delta(^{19}F) = -86.6$, a meridional configuration with regard to the pentafluoroethyl groups is postulated. This structure could be proven by a single-crystal structure analysis.

The compound crystallizes in the triclinic space group $P\bar{1}$ with two formula units per unit cell (cf. Figure 4).[16] One

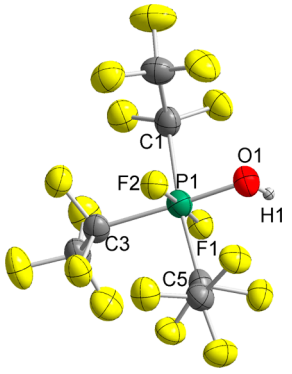
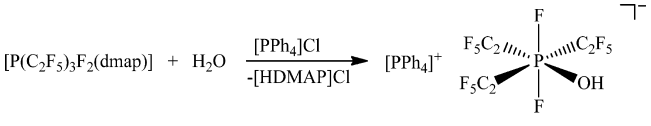


Figure 4. Molecular structure and numbering scheme of the $[P(C_2F_5)_3F_2OH]^-$ ion as its $[PPh_4]^+$ salt. 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: P1–F1 163.0(2), P1–F2 162.9(2), P1–O1 164.7(3), P1–C1 195.9(4), P1–C3 197.8(4); F1–P1–F2 176.4(1), O1–P1–C5 175.1(2).

$[PPh_4][P(C_2F_5)_3F_2OH]$ unit represents the asymmetric unit. The general molecular structure of the anion resembles that of $[P(C_2F_5)_3F_2(dmap)]$. The proton of the hydroxy function (H1) is directed at a fluorine atom of the difluoromethylene unit of a neighboring anion. The H1–O1–P1–F2 dihedral angle of 22.4° is a consequence of weak intermolecular contact. Quantum chemical calculations at the B3LYP/6-311G+(2d,p)[18] level of theory favor a C_s symmetrical conformation and therefore a H1–O1–P1–F2 dihedral angle of 0°. In general, the structural parameters are described well by quantum chemical calculations. The P–O distance of 164.7 pm represents a classical single bond.[19]

An acetato ligand is introduced by the reaction of $[P(C_2F_5)_3F_2(dmap)]$ with acetic acid (HOAc) or acetic anhydride. In the case of acetic acid, the product $[HDMAP][P(C_2F_5)_3F_2OAc]$ is isolated as a colorless solid in a yield of 93% and fully characterized by multinuclear NMR spectroscopy. The reaction with acetic anhydride, yielding $[P(C_2F_5)_3F_2OAc]^-$ and concluding the formation of the amide $[AcDMAP]^+$, shows that the acidic hydrogen atom in HX is not necessarily required for this reaction.



The precursor $[P(C_2F_5)_3F_2(dmap)]$ is reacted with phenol, yielding the corresponding phenolatophosphate $[HDMAP][P(C_2F_5)_3F_2OPh]$ as a room-temperature ionic liquid.

The treatment of $[P(C_2F_5)_3F_2(dmap)]$ with 0.5 equivalents of hydroquinone in diethyl ether furnishes $[HDMAP]_2[\{P(C_2F_5)_3F_2O\}_2C_6H_4]$ as a colorless solid. Results of an elemental analysis as well as an electrospray ionization (ESI) mass

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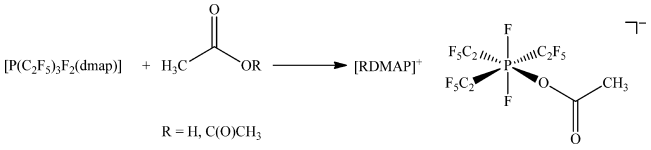
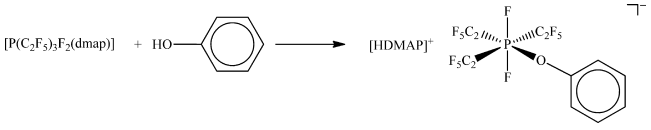


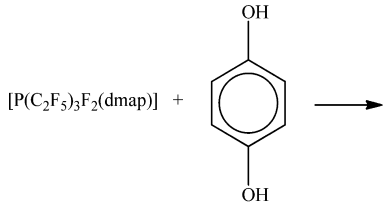
spectrum (negative scan mode) confirm the formation of the doubly charged diphosphate anion $[\{P(C_2F_5)_3F_2O\}_2C_6H_4]^{2-}$.

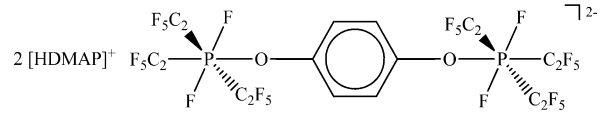


For $[HDMAP][P(C_2F_5)_3F_2OPh]$ as well as for $[HDMAP]_2[\{P(C_2F_5)_3F_2O\}_2C_6H_4]$, only one resonance is detected spectroscopically by NMR for the fluorine atoms directly bound to the phosphorus atom. The chemical shift of around $\delta(^{19}F) = -86$ favors a meridional configuration with regard to the pentafluoroethyl groups, which is confirmed for some $[P(C_2F_5)_3F_2X]$ derivatives (X = OH, DMAP, OEt) by single-crystal structure analyses.

Our knowledge of alkoxypentafluorophosphates is scarce. Riesel and Kant reported in 1985 the synthesis of ethoxypentafluorophosphate $[PF_5OEt]^-$, which was obtained by the reaction of PCl_5 with HF and ethanol in the presence of triethylamine.[20]

The reaction of $[P(C_2F_5)_3F_2(dmap)]$ with ethanol in diethyl ether selectively leads to the corresponding ethoxyphosphate $[HDMAP][P(C_2F_5)_3F_2OEt]$. The product is isolated in a 100% yield as a colorless solid by removing the solvent in vacuum (mp 75−78 °C).





By NMR spectroscopy, only one resonance at $\delta(^{19}F) = -94.5$ is detected for the fluorine atoms F_A bound directly to the phosphorus atom. This is in accordance with a trans orientation of the fluorine atoms at the phosphorus atom.

The product crystallizes in the monoclinic space group $P2_1/n$ with four formula units per unit cell.[16] The proton H1 at the nitrogen atom of the pyridine ring is aligned with the oxygen atom O1 of the ethoxy group (cf. Figure 5) with an O−N distance of 312.9 pm, which is consistent with the sum of the van der Waals radii of 310 pm.[17] This shows that the introduction of an oxygen-bound functional group increases the coordination properties of the anion. The C5−P−F1 angle of 83.7° is significantly compressed by a strong interaction of the fluorine atom F1 with the electron lone pairs of the oxygen atom.

To investigate the influence of electron-withdrawing substituents on the physical properties of the corresponding phosphate anion, $[P(C_2F_5)_3F_2(dmap)]$ was treated with

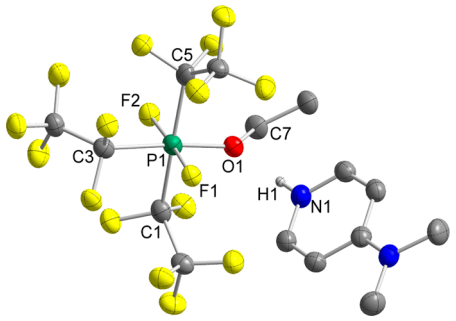
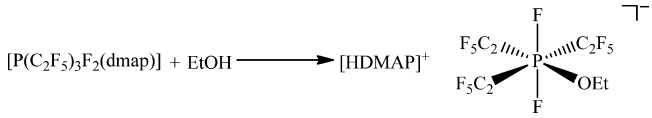


Figure 5. Molecular structure and numbering scheme of $[HDMAP][P(C_2F_5)_3F_2OEt]$. All carbon bonded hydrogen atoms are omitted for clarity. 50% probability amplitude displacement ellipsoids are shown. Selected bond lengths [pm] and angles [deg]: P1−F1 164.2(2), P1−F2 162.9(2), P1−O1 166.2(2), P1−C1 195.7(3), P1−C3 198.4(3); F1−P1−F2 175.8(1), F1−P1−C3 83.7(1), O1−P1−C3 169.8(1).

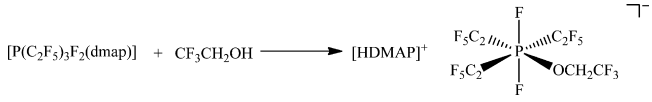
trifluoroethanol. The product $[HDMAP][P(C_2F_5)_3F_2OCH_2CF_3]$ was isolated in a yield of 95% after removing the solvent in vacuum (mp 91−93 °C).

The ligation of the trifluoroethoxy group to the $(C_2F_5)_3PF_2$ moiety is evident by the observation of a $^3J_{P,H}$ coupling of $J = 4$ Hz in the ^{1}H NMR spectrum.



After a cation exchange of both $[HDMAP][P(C_2F_5)_3F_2OEt]$ and $[HDMAP][P(C_2F_5)_3F_2OCH_2CF_3]$ by means of 1-butyl-2,3-dimethylimidazolium chloride ([BMMIm]Cl), the products $[BMMIm][P(C_2F_5)_3F_2OEt]$ and $[BMMIm][P(C_2F_5)_3F_2OCH_2CF_3]$ were obtained in yields of 87−91% as ionic liquids with melting points below room temperature. Their properties were investigated by differential scanning calorimetry (DSC) analysis. Both compounds exhibit a glass transition at about −57 °C. The decomposition points differ significantly. While the ethoxy derivative decomposes already at 120 °C, $[BMMIm][P(C_2F_5)_3F_2OCH_2CF_3]$ is stable up to 212 °C.

To synthesize a difluorotris(pentafluoroethyl)phosphate with an additional functional group, $[P(C_2F_5)_3F_2(dmap)]$ was dissolved in diethyl ether and treated with an excess of 1,2-ethanediol. In parallel to the desired formation of $[HDMAP][P(C_2F_5)_3F_2OC_2H_4OH]$, a ring closure under liberation of C_2F_5H could not be excluded a priori. Under the chosen reaction conditions, this side reaction could not be observed. The product $[HDMAP][P(C_2F_5)_3F_2OC_2H_4OH]$ was obtained in a 89% yield as a colorless solid. It decomposes at 91 °C.



Summary of NMR Spectroscopic Data. The chemical shift of $[P(C_2F_5)_3F_2X]^-$ derivatives in the ^{31}P NMR spectrum ranges from $\delta(^{31}P) = -145$ to -155 with a characteristic coupling pattern. The signal is split into a triplet due to the $^1J_{P,F}$ coupling to the fluorine atoms directly bound to the phosphorus atom. Thereby coupling constants range from 846 Hz for $[P(C_2F_5)_3F_2OH]^-$ to 986 Hz for $[P(C_2F_5)_3F_2(dmap)]$. An additional quintet-of-triplets splitting results from the $^2J_{P,F}$ coupling to the fluorine atoms of the CF_2 units,

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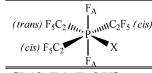
which are in cis and trans positions relative to the functional substituent X.

The ^{19}F NMR spectra of difluorotris(pentafluoroethyl)-phosphate derivatives can be divided generally into three regions (cf. Table 1). (A) Both resonances of the cis- and trans-

Table 1. Selected NMR Spectroscopic Data for $[P(C_2F_5)_3F_2X]$ Derivatives with Increasing Coupling Constant $^1J(PF_A)$

	$\delta(^{19}F)$ (F_A)	$^1J_{P,FA}$ [Hz]	$^2J_{P,Fcis}$ [Hz]	$^2J_{P,Ftrans}$ [Hz]
$[P(C_2F_5)_3F_2OH]^-$	-86,6	846	86	86
$[P(C_2F_5)_3F_2OEt]^-$	-94,5	869	86	83
$[P(C_2F_5)_3F_2OC_2H_4OH]^-$	-93,2	873	83	83
$[\{P(C_2F_5)_3F_2O\}_2C_6H_4]^{2-}$	-86,9	881	96	78
$[P(C_2F_5)_3F_2OCH_2CF_3]^-$	-93,8	885	88	88
$[P(C_2F_5)_3F_2OPh]^-$	-85,5	896	98	84
$[P(C_2F_5)_3F_2OAc]^-$	-86,9	923	103	84
$[P(C_2F_5)_3F_2(dmap)]$	-99,4	986	107	97

positioned CF_3 units are detected around −80 ppm and assigned to the respective C_2F_5 groups on the basis of their integrals of 2:1. (B) The signals of the CF_2 units are observed in a range from −110 to −125 ppm and assigned on the basis of their integrals as well as their $^2J_{P,F}$ coupling constants. However, on the basis of the chemical shift or the coupling pattern alone, no statement can be made about the respective substituent X. (C) Characteristic of the substituent X is the chemical shift of the fluorine atoms bound directly to the phosphorus atom as well as the corresponding $^1J_{P,F}$ coupling constant. Trans positioned fluorine atoms exhibit a chemical shift in a range of −80 to −100 ppm for the discussed neutral and negatively charged $[P(C_2F_5)_3F_2X]$ derivatives.

CONCLUSIONS

To develop the chemistry of weakly coordinating anions derived from $[P(C_2F_5)_3F_3]^-$, which is ideally suited for an application as ionic liquid, functional substituents X (X = OH, OAlkyl, OAryl, OAcyl) were attached to the phosphorane moiety $(C_2F_5)_3PF_2$. The reaction of the Lewis acid $(C_2F_5)_3PF_2$ with DMAP quantitatively afforded the corresponding adduct $[P(C_2F_5)_3F_2(dmap)]$. This adduct offers an access to the corresponding phosphate anions $[P(C_2F_5)_3F_2X]^-$ when treated with Brønsted acids (HX). The proton was trapped by the liberated base DMAP. This allows the one-step introduction of a OH substitution into WCAs. Bifunctional diols can be substituted selectively once or twice, depending on the stoichiometry employed. The corresponding $[PPh_4]$ salts are isolated as solids, whereas the corresponding imidazolium salts were obtained as room-temperature ionic liquids. $[P(C_2F_5)_3F_2X]^-$ derivatives with partially fluorinated substituents exhibit an increased thermal stability with regard to their nonfluorinated counterparts.

EXPERIMENTAL SECTION

$(C_2F_5)_3PF_2$ and $(C_4F_9)_3PF_2$ were provided by the Merck KGaA company, Darmstadt, Germany. $(C_2F_5)_2PF_3$ was prepared according to the protocol described in the patent application.[21] All other chemicals were obtained from commercial sources and used without further purification. Standard high-vacuum techniques were employed throughout all preparative procedures. Nonvolatile compounds were handled in a dry N_2 atmosphere using Schlenk techniques.

NMR spectra were recorded at room temperature with a Bruker Avance II 300 spectrometer (^1H: 300.13 MHz; ^{13}C: 75.47 MHz; ^{19}F: 282.40 MHz; ^{31}P: 111.92 MHz) with positive shifts being downfield from the external standards [85% orthophosphoric acid (^{31}P), CCl_3F (^{19}F), and tetramethylsilane (^1H, ^{13}C)].

Melting points were determined by using an HWS Mainz 2000 apparatus. C, H, and N analyses were carried out with a HEKAtech Euro EA 3000 apparatus. Electron ionization (EI) (20 eV) and ESI mass spectra were recorded with a Finnigan MAT 900 S spectrometer.

The moisture content of ionic liquids was measured by a Karl Fischer titration (831 KF-Coulometer, Metrohm), and the content of chloride and fluoride ions was measured by ion chromatography (830 Metrohm). The thermal stability (DSC) of ionic liquids was measured using a Netzsch DSC 204.

Data collection for X-ray structure determination of $[P(C_2F_5)_3F_2(dmap)]$, $[PPh_4][P(C_2F_5)_3F_2OH]$, and $[HDMAP][P(C_2F_5)_3F_2OEt]$ was performed on a STOE IPDS II diffractometer using graphite-monochromated Mo Kα radiation (71.073 pm). The data were corrected for Lorentz and polarization effects. A numerical absorption correction based on crystal-shape optimization was applied for all data (X-Shape 2.01, Crystal Optimisation for Numerical Absorption Correction, STOE & Cie GmbH, Darmstadt, 2001). The programs used herein are Stoe's X-Area (X-Area 1.16, STOE & Cie GmbH Darmstadt, 2003), including X-RED and X-Shape for data reduction and numerical absorption correction (X-RED32 1.03, Stoe Data Reduction Program, Stoe & Cie GmbH, Darmstadt, 2002), and X-Step32 program (X-STEP32 1.06f, Stoe & Cie GmbH, Darmstadt, 2000), including SHELXS-97 (G. M. Sheldrick, SHELXS-97, University of Göttingen, 1998) and SHELXL-97 (G. M. Sheldrick, SHELXL-97, University of Göttingen, 1997) for structure solution and refinement. All hydrogen atoms were placed in idealized positions using a riding model. The last refinement cycles included atomic positions for all atoms, anisotropic thermal parameters for all non-hydrogen atoms, and isotropic thermal parameters for all hydrogen atoms.

Synthesis of $[P(C_2F_5)_3F_2(dmap)]$. $(C_2F_5)_3PF_2$ (12.2 g, 28.6 mmol) was added slowly to a suspension of 4-dimethylaminopyridine (2.8 g, 22.9 mmol) in diethyl ether (100 mL). After stirring for 15 min, all volatile compounds were removed in vacuo. A colorless solid remained (12.1 g, 97%), mp 150−153 °C. ^1H NMR (300.1 MHz, $CDCl_3$): δ = 3.2 (s, 6H, CH_3), 6.7 (d, $^3J_{H,H}$ = 7 Hz, 1H), 8.4 (m, 1H) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$): δ = 38.6 (s, CH_3), 105.9 (s, C1), 138.9 (s, C2), 156.1 (s, C3) ppm; $^{13}C\{^{19}F\}$ NMR (75.5 MHz, $CDCl_3$): δ = 116.7 (m, CF_2), 118.2 (m, CF_3) ppm; ^{19}F NMR (282.4 MHz, $CDCl_3$): δ = −80.4 (m, *trans*-CF_3), −81.6 (m, *cis*-CF_3), −99.4 (d, $^1J_{P,F}$ = 986 Hz, PF_2), −111.5 (m, *cis*-CF_2), −115.3 (d, m, $^2J_{P,F}$ = 95 Hz, *trans*-CF_2) ppm; ^{31}P NMR (111.9 MHz, $CDCl_3$): δ = −144.5 (t, quin, t, $^1J_{P,F}$ = 986 Hz, $^2J_{P,Fcis}$ = 107 Hz, $^2J_{P,Ftrans}$ = 97 Hz) ppm. Elemental analysis (%) calcd: N 5.11, C 28.48, H 1.84; found: N 4.91, C 28.63, H 1.67. Mass spectrum (EI, 20 eV) {*m*/*z* (%) [assignment]}: 407 (12) $[M]^+$, 307 (50) $[M\text{-}C_2F_5]^+$, 207 (15) $[M\text{-}2\ C_2F_5]^+$, 122 (100) $[C_7H_{10}N_2]^+$, 69 (6) $[CF_3]^+$.

Synthesis of $[PPh_4][P(C_2F_5)_3F_2OH]$. $[P(C_2F_5)_3F_2(dmap)]$ (0.96 g, 1.75 mmol) was dissolved in diethyl ether and treated with an excess of water. After stirring for 30 min, $[PPh_4]Cl$ (0.66 g, 1.75 mmol), dissolved in water (2 mL), was added and stirred for 20 min. The organic phase was separated and extracted three times with water. The organic phase was freed from solvent in vacuo. A colorless solid remained (1.29 g, 94%), mp 139 °C. ^1H NMR (300.1 MHz, CD_3CN): δ = 5.1 (t, d, $^3J_{F,H}$ = 14 Hz, $^2J_{P,H}$ = 3 Hz, 1 H, PO*H*), 7.8−8.1 (m, 20 H, $CH_{arom.}$) ppm; $^{13}C\{^1H\}$ NMR (75.5 MHz, CD_3CN): δ = 118.5 (d, $^1J_{P,C}$ = 90 Hz, C1), 130.3 (d, $^2J_{P,C}$ = 13 Hz, C2), 134.7 (d, $^3J_{P,C}$ = 10 Hz, C3), 135.4 (d, $^4J_{P,C}$ = 3 Hz, C4) ppm; $^{13}C\{^{19}F\}$ NMR (75.5 MHz, CD_3CN): δ = 119.1 (m, CF_2), 120.7 (m, CF_3) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.1 (m, *trans*-CF_3), −81.2 (m, *cis*-CF_3), −86.6 (d, $^1J_{P,F}$ = 846 Hz, PF_2), −114.1 (d, $^2J_{P,F}$ = 86 Hz, CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = 23.2 (s, $[PPh_4]^+$), −148.3 (t, sept, $^1J(PF)$ = 845 Hz, $^2J_{P,F}$ = 86 Hz) ppm. Elemental analysis (%) calcd: C 46.05, H 2.71; found: C 46.40, H 2.79. ESI mass spectrum in the negative

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range (neg.) {m/z (%) [assignment]}: 443.2 (100) $[M]^-$, 323.2 (41) $[P(C_2F_5)_2F_2O]^-$.

Synthesis of [HDMAP][P(C$_2$F$_5$)$_3$F$_2$OAc]. A sample of $[P(C_2F_5)_3F_2(dmap)]$ (0.52 g, 0.96 mmol) was treated in dichloromethane with acetic acid (HOAc; 0.19 g, 3.17 mmol) and stirred at room temperature for 3 h. After removing volatile compounds in vacuo, a colorless solid remained (0.54 g, 93%). ^{1}H NMR (300.1 MHz, CD_3CN): δ = 1.9 (s, 3 H, OC(O)CH_3), 3.2 (s, 6 H, N(CH_3)$_2$), 6.9 (d, $^3J_{H,H}$ = 7 Hz, 1 H, H1), 7.9 (d, $^3J_{H,H}$ = 7 Hz, 1 H, H2) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 23.3 (s, OC(O)CH_3), 39.6 (s, N(CH_3)$_2$), 107.1 (s, C1), 138.6 (s, C2), 157.7 (s, C3), 166.3 (d, $^2J_{P,C}$ = 18 Hz, OC(O)CH_3) ppm; ^{13}C{^{19}F} NMR (75.5 MHz, CD_3CN): δ = 116.7 (m, CF_2), 120.0 (m, CF_3) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.2 (m, *trans*-CF_3), −81.8 (m, *cis*-CF_3), −86.9 (d, m, $^1J_{P,F}$ = 923 Hz, PF_2), −115.3 (d, m, $^2J_{P,F}$ = 85 Hz, *trans*-CF_2), −116.0 (d, m, $^2J_{P,F}$ = 103 Hz, *cis*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −146.3 (t, quin, t, $^1J_{P,F}$ = 915 Hz, $^2J_{P,Fcis}$ = 103 Hz, $^2J_{P,Ftrans}$ = 84 Hz) ppm.

Synthesis of [HDMAP][P(C$_2$F$_5$)$_3$F$_2$OPh]. $[P(C_2F_5)_3F_2(dmap)]$ (0.52 g, 0.95 mmol) was dissolved in diethyl ether and treated with phenol (0.13 g, 1.34 mmol). After stirring for 12 h, two phases had formed. The solvent was removed in vacuo, and a colorless liquid remained. ^{1}H NMR (300.1 MHz, CD_3CN): δ = 3.4 (s, 6 H, CH_3), 6.7 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H1), 7.1 (m, 5H, OC_6H_5), 8.3 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H2) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 39.7 (s, CH_3), 106.9 (s, C1), 115.2 (s, C5), 120.4 (s, C6/7), 128.9 (s, C6/7), 138.8 (s, C2), 157.0 (s, C4), 157.6 (s, C3) ppm; ^{13}C{^{19}F} NMR (75.5 MHz, CD_3CN): δ = 118.1 (m, CF_2), 119.7 (m, CF_3) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −79.4 (m, *trans*-CF_3), −80.5 (m, *cis*-CF_3), −85.5 (d, m, $^1J_{P,F}$ = 896 Hz, PF_2), −111.5 (d, m, $^2J_{P,F}$ = 97 Hz, *cis*-CF_2), −112.7 (d, m, $^2J_{P,F}$ = 79 Hz, *trans*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −147.5 (t, quin, t, $^1J_{P,F}$ = 893 Hz, $^2J_{P,Fcis}$ = 98 Hz, $^2J_{P,Ftrans}$ = 84 Hz) ppm.

Synthesis of [HDMAP]$_2$[{P(C$_2$F$_5$)$_3$F$_2$O}$_2$C$_6$H$_4$]. $[P(C_2F_5)_3F_2(dmap)]$ (1.11 g, 2.0 mmol) was dissolved in diethyl ether and treated with hydroquinone (0.11 g, 1.0 mmol). After stirring for 4 h, volatile compounds were removed in vacuo. A colorless solid remained (0.85 g, 78%). ^{1}H NMR (300.1 MHz, CD_3CN): δ = 3.1 (s, 6 H, CH_3), 6.8 (m, 4 H, H4/5), 6.8 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H2), 7.9 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H2) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.4 (m, *trans*-CF_3), −81.6 (m, *cis*-CF_3), −86.9 (d, m, $^1J_{P,F}$ = 881 Hz, PF_2), −112.9 (d, m, $^2J_{P,F}$ = 98 Hz, *cis*-CF_2), −113.9 (d, m, $^2J_{P,F}$ = 80 Hz, *trans*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −148.0 (t, quin, t, $^1J_{P,F}$ = 882 Hz, $^2J_{P,Fcis}$ = 96 Hz, $^2J_{P,Ftrans}$ = 78 Hz) ppm. Elemental analysis (%) calcd: N 4.67, C 32.07, H 1.51; found: N 4.73, C 32.40, H 2.26.

Synthesis of [HDMAP][P(C$_2$F$_5$)$_3$F$_2$OEt]. Ethanol (10.6 g, 230 mmol), dissolved in diethyl ether (100 mL), was treated with $[P(C_2F_5)_3F_2(dmap)]$ (12.5 g, 23 mmol) and stirred for 30 min. Volatile compounds were removed overnight in vacuo. A colorless solid remained (13.6 g, 100%), mp 75−78 °C. ^{1}H NMR (300.1 MHz, CD_3CN): δ = 1.1 (t, d, $^3J_{H,H}$ = 7 Hz, $^4J_{P,H}$ = 1 Hz, 3 H, OCH_2CH_3), 3.2 (s, 6 H, CH_3), 4.0 (m, $^3J_{P,H}$ = 7 Hz, $^3J_{H,H}$ = 7 Hz, 2 H, OCH_2CH$_3$), 5.3 (s, 1 H, NH^+), 6.8 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H1), 8.0 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H2) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 16.0 (d, $^3J_{C,P}$ = 10 Hz, OCH_2CH_3), 39.6 (s, N(CH_3)$_2$), 61.8 (m, OCH_2CH$_3$), 107.1 (s, C1), 138.5 (s, C2), 157.0 (s, C4), 157.9 (s, C3) ppm; ^{13}C{^{19}F} NMR (75.5 MHz, CD_3CN): δ = 118.8 (m, CF_2), 122.5 (m, CF_3) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.6 (m, *trans*-CF_3), −81.8 (m, *cis*-CF_3), −94.5 (d, m, $^1J_{P,F}$ = 869 Hz, PF_2), −113.5 (d, m, $^2J_{P,F}$ = 83 Hz, *trans*-CF_2), −114.4 (d, m, $^2J_{P,F}$ = 86 Hz, *cis*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −149.4 (t, sept, $^1J_{P,F}$ = 869 Hz, $^2J_{P,F}$ = 88 Hz) ppm. Elemental analysis (%) calcd: N 4.71, C 30.32, H 2.71; found: N 4.74, C 30.32, H 2.69. ESI mass spectrum in the negative range (neg.) {m/z (%) [assignment]}: 965.0 (9) $[NaM_2]^-$, 471.2 (100) $[M]^-$, 445.1 (21) $[P(C_2F_5)_3F_3]^-$.

Synthesis of [HDMAP][P(C$_2$F$_5$)$_3$F$_2$OCH$_2$CF$_3$]. $[P(C_2F_5)_3F_2(dmap)]$ (2.5 g, 4.5 mmol) was dissolved in diethyl ether and treated with trifluoroethanol (0.9 g, 9.0 mmol). After stirring for 12 h, volatile compounds were removed in vacuo. A colorless solid remained (2.8 g, 95%), mp 91−93 °C. ^{1}H NMR (300.1 MHz, CD_3CN): δ = 3.2 (s, 6 H, CH_3), 4.4 (quar, d, $^3J_{F,H}$ = 9 Hz, $^3J_{P,H}$ = 4 Hz, 2 H, OCH_2CF$_3$), 6.8 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H1), 8.0 (d, $^3J_{H,H}$ = 7 Hz, 2 H, H2) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 39.6 (s, N(CH_3)$_2$), 64.1 (m, OCH_2CF$_3$), 106.9 (s, C1), 138.9 (s, C2), 157.7 (s, C3) ppm; ^{13}C{^{19}F} NMR (75.5 MHz, CD_3CN): δ = 118.8 (m, CF_2), 120.4 (m, CF_3), 124.5 (m, OCH_2CF$_3$) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −75.4 (s, OCH_2CF_3), −79.6 (m, *trans*-CF_3), −80.8 (m, *cis*-CF_3), −93.8 (d, m, $^1J_{P,F}$ = 883 Hz, PF_2), −112.2 (d, m, $^2J_{P,F}$ = 88 Hz, CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −149.9 (t, sept, $^1J_{P,F}$ = 886 Hz, $^2J_{P,F}$ = 88 Hz) ppm. Elemental analysis (%) calcd: N 4.32, C 27.79, H 2.02; found: N 4.47, C 28.10, H 1.64. ESI mass spectrum in the negative range (neg.) {m/z (%) [assignment]}: 1088.9 (13) $[KM_2]^-$, 525.2 (100) $[M]^-$.

Synthesis of [BMMIm][P(C$_2$F$_5$)$_3$F$_2$OEt]. [HDMAP][$P(C_2F_5)_3F_2$OEt] (5.3 g, 9 mmol) was dissolved in dichloromethane (50 mL) and treated with 1-butyl-2,3-dimethylimidazolium chloride (1.7 g, 9 mmol) dissolved in dichloromethane (5 mL). After stirring for 2 h, the organic phase was separated and extracted three times with water. Volatile compounds of the organic phase were removed in vacuo. A colorless liquid remained (4.9 g, 87%). ^{1}H NMR (300.1 MHz, CD_3CN): δ = 0.9 (t, $^3J_{H,H}$ = 7 Hz, 3 H, H9/13), 1.0 (t, $^3J_{H,H}$ = 7 Hz, 3 H, H13/9), 1.3 (sext, $^3J_{H,H}$ = 8 Hz, 2 H, H8), 1.7 (quin, $^3J_{H,H}$ = 7 Hz, 2 H, H7), 2.5 (s, 3 H, H11), 3.7 (s, 3 H, H10), 3.9 (m, 4 H, H6/H12), 7.2 (m, 2 H, H4/H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 9.0 (s, C11), 12.7 (s, C9), 16.0 (s, C13), 19.1 (s, C8), 31.2 (s, C7), 34.7 (s, C10), 48.0 (s, C6), 61.8 (s, C12), 120.8 (s, C4/5), 122.2 (s, C5/4), 144.3 (s, C2) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −80.1 (m, *trans*-CF_3), −81.3 (m, *cis*-CF_3), −93.9 (d, m, $^1J_{P,F}$ = 870 Hz, PF_2), −113.3 (d, m, $^2J_{P,F}$ = 84 Hz, *trans*-CF_2), −116.9 (d, m, $^2J_{P,F}$ = 86 Hz, *cis*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −149.5 (t, sept, $^1J_{P,F}$ = 866 Hz, $^2J_{P,F}$ = 84 Hz) ppm.

Synthesis of [BMMIm][P(C$_2$F$_5$)$_3$F$_2$OCH$_2$CF$_3$]. [HDMAP]-$[P(C_2F_5)_3F_2OCH_2CF_3]$ (4.7 g, 7.3 mmol) was dissolved in dichloromethane (50 mL) and treated with 1-butyl-2,3-dimethylimidazolium chloride (1.4 g, 7.4 mmol) dissolved in dichloromethane (3 mL). After stirring for 1 h, the organic phase was separated and extracted three times with water. Volatile compounds of the organic phase were removed in vacuo. A colorless liquid remained (4.5 g, 91%). ^{1}H NMR (300.1 MHz, CD_3CN): δ = 0.9 (t, $^3J_{H,H}$ = 7 Hz, 3 H, H9), 1.3 (sext, $^3J_{H,H}$ = 8 Hz, 2 H, H8), 1.7 (quin, $^3J_{H,H}$ = 7 Hz, 2 H, H7), 2.5 (s, 3 H, H11), 3.7 (s, 3 H, H10), 4.0 (t, $^3J_{H,H}$ = 7 Hz, 2 H, H6), 4.4 (m, 2 H, H12), 7.2 (m, 2 H, H4/H5) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 9.0 (s, C11), 12.7 (s, C9), 19.1 (s, C8), 31.2 (s, C7), 34.7 (s, C10), 48.0 (s, C6), 64.2 (m, C12), 120.8 (s, C4/5), 122.3 (s, C5/4), 124.5 (m, C13), 144.8 (s, C2) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −75.9 (s, 3F, −OCH_2CF_3), −80.3 (m, 3F, *trans*-CF_3), −81.7 (m, 6F, *cis*-CF_3), −94.5 (d, m, $^1J_{P,F}$ = 884 Hz, 2F, PF_2), −113.4 (m, 6F, *cis*-, *trans*-CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −149.9 (t, sept, $^1J_{P,F}$ = 885 Hz, $^2J_{P,F}$ = 85 Hz) ppm.

Synthesis of [HDMAP][P(C$_2$F$_5$)$_3$F$_2$OC$_2$H$_4$OH]. A sample of $[P(C_2F_5)_3F_2(dmap)]$ (0.60 g, 1.1 mmol) was dissolved in diethyl ether and treated with ethanediol (0.10 g, 1.6 mmol). After stirring for 24 h, volatile compounds were removed in vacuo. A colorless solid remained (0.61 g, 89%), mp 88 °C (decomposition: 91 °C). ^{1}H NMR (300.1 MHz, CD_3CN): δ = 3.2 (s, 6H, CH_3), 3.5 (t, $^3J_{H,H}$ = 4 Hz, 2 H, H5), 4.0 (d, t, $^3J_{P,H}$ = 4 Hz, $^3J_{H,H}$ = 4 Hz, 2 H, H4), 6.8 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H1), 8.0 (d, $^3J_{H,H}$ = 8 Hz, 2 H, H2) ppm; ^{13}C{^{1}H} NMR (75.5 MHz, CD_3CN): δ = 39.6 (s, N(CH_3)$_2$), 62.1 (d, $^2J_{P,C}$ = 9 Hz, C4), 67.8 (s, C5), 106.8 (s, C1), 138.6 (s, C2), 157.6 (s, C3) ppm; ^{13}C{^{19}F} NMR (75.5 MHz, CD_3CN): δ = 116.7 (m, CF_2), 120.6 (m, CF_3), 124.5 (m, OCH_2CF$_3$) ppm; ^{19}F NMR (282.4 MHz, CD_3CN): δ = −79.3 (m, *trans*-CF_3), −80.4 (m, *cis*-CF_3), −93.2 (d, m, $^1J_{P,F}$ = 873 Hz, PF_2), −112.6 (d, m, $^1J_{P,F}$ = 83 Hz, CF_2) ppm; ^{31}P NMR (111.9 MHz, CD_3CN): δ = −149.2 (t, sept, $^1J_{P,F}$ = 871 Hz, $^2J_{P,F}$ = 86 Hz) ppm. Elemental analysis (%) calcd: N 4.59, C 29.52, H 2.64; found: N 4.62, C 29.54, H 2.28.

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■ ASSOCIATED CONTENT

Supporting Information

Results of DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org. CCDC 971886 ($[PPh_4][P(C_2F_5)_3F_2OH]$), CCDC 971887 ($[P(C_2F_5)_3F_2(dmap)]$), and CCDC 971888 ($[HDMAP][P(C_2F_5)_3F_2OEt]$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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(16) Data for $[P(C_2F_5)_3F_2(dmap)]$: colorless crystal, M_r = 548.20, monoclinic, space group $P2_1/c$, a = 9.852(1) Å, b = 16.814(1) Å, c = 11.826(1) Å, β = 110.31(1)°, V = 1837.2(3) Å^3, Z = 4, $F(000)$ = 1080; 28 196 reflections up to θ = 29.7° collected, 5148 independent reflections, thereof 4009 with $I > 2\sigma(I)$, 302 parameters. R values: R_1 = 0.037 for refl. with $I > 2\sigma(I)$, wR_2 = 0.103 for all data. Data for $[PPh_4][P(C_2F_5)_3F_2OH]$: colorless crystal, M_r = 782.41, triclinic, space group $P\bar{1}$, a = 10.654(2) Å, b = 12.364(2) Å, c = 13.811(2) Å, α = 63.56(1)°, β = 73.57(1)°, γ = 77.74(1)°, V = 1554.5(5) Å^3, Z = 2, $F(000)$ = 784; 16951 reflections up to θ = 27.4° collected, 6886 independent reflections, thereof 4005 with $I > 2\sigma(I)$, 453 parameters. R values: R_1 = 0.061 for refl. with $I > 2\sigma(I)$, wR_2 = 0.189 for all data. Data for $[HDMAP][P(C_2F_5)_3F_2OEt]$: colorless crystal, M_r = 594.27, monoclinic, space group $P2_1/n$, a = 7.945(1) Å, b = 15.662(2) Å, c = 17.246(3) Å, β = 95.19(1)°, V = 2137.2(6) Å^3, Z = 4, $F(000)$ = 1184; 19 082 reflections up to θ = 27.0° collected, 4653 independent reflections, thereof 2458 with $I > 2\sigma(I)$, 332 parameters. R values: R_1 = 0.036 for refl. with $I > 2\sigma(I)$, wR_2 = 0.073 for all data. Additional crystallographic data are available in the Supporting Information.

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